



# Pyrolytical Sifting of Poly (styrene-co-methyl methacrylate) Blended with Stannic Chloride: An Investigation Engaging IR and Py-GC-MS Techniques

M. Arshad<sup>1\*</sup>

<sup>1</sup>Chemistry Division, PINSTECH, Nilore, Islamabad, Pakistan.

## Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

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## ABSTRACT

Pyrolytic study of copolymer, i. e., P(S-co-MMA) blended with SnCl<sub>4</sub> was performed using inert atmosphere. Five different proportions of polymer-additive blends (additive ratio from 2.5% to 12.5%) were formulated using a common solvent, i. e., acetone. Thermal degradations proceed with two-stage for neat copolymer and three-stage for blends and additive alike. Residue was observed only for additive. Thermoanalytical scrutiny of these blends reveals that copolymer is more stable than blends (when T<sub>o</sub> = temperature at which first mass-loss is detected, is compared), however, blends appear more stable than copolymer on the basis of their T<sub>max</sub> (temperature at which maximum mass-loss is observed). Chlorobenzene, 1,2-dichlorobenzene, 1-chlorostyrene,  $\alpha$ -methylstyrene, etc. were believed to be the outcome of interaction between the copolymer and the additive. The arising of benzene, although one of the degradation products of the neat copolymer, was linked with the influence of additive on copolymer due to its increased amount. Chlorine (free radicals) initiated the early degradation of the copolymer (after being generated by the decomposition of the additive) and also appeared as a 'pendent element' to the compounds consisting of few carbon units (short chain entities). In the whole study, the degradation of styrene

\*Corresponding author: E-mail: [marshads53@yahoo.com.sg](mailto:marshads53@yahoo.com.sg);

units does not end in oligomers. The effectiveness of additive regarding flame retardance furnished a linear trend as HBR (horizontal burning rate) which indicated that higher the concentration of additive in the blend, lower was the burning rate and this also confirmed the homogeneous spread of additive in the neat copolymer.

*Keywords: P(S-co-MMA); stannic chloride; thermoanalytical methods; IR spectroscopy; GC-MS characterization.*

## 1. INTRODUCTION

In continuation of our previous studies, we have investigated the thermal behavior of homopolymer, i. e., poly(methyl methacrylate) in the presence of tin (IV) chloride. Instead of physical mixing of polymer-additive, the films were cast employing acetone as common solvent for five different proportions—polymer to additive. The complex formation between additive and carbonyl oxygen (pendent groups of MMA units) of homopolymer was observed in the films soon after the mixing of the components in the blends. The thermoanalytical probe revealed that blends started degrading at a temperature lower than that of the neat polymer and higher than that of the pure additive [1].

Many compounds, organic as well as inorganic [2-5] were utilized, either at molecular level or as powdered mixtures, to enhance the stability and to change the mode of degradation of polymers/copolymers during fire (high temperatures). Polymer mixtures have also been examined thermally to determine their mode of decomposition [6,7]. One of the studies [7] describes that the mixture (PMMA and PS in the form of thin film) may not exhibit any detectable interaction between the polymers while the presence of S (styrene) exerts disproportionate stabilizing effect on the methyl methacrylate polymer chain keeping in view the behavior of the copolymer as being between that of the individual homopolymers. The introduction of different functional groups in polymers is another mode which has proved valuable [8]. It is revealed through limiting oxygen indices that phosphorated polymers have potential fire retardant properties. The search for other avenues in this direction has been flourishing for many years.

Our interest on this aspect has produced several publications [9-19] ranging from thermal degradation of polymers/copolymer to the pyrolysis of mixtures of polymers/copolymers with organometallic substances and blends (molecular-level mixing—films cast from common

solvent) of polymer with purely inorganic salts. For copolymers, it was noticed that even the presence of 10 mol % of styrene in the system, phenyl methacrylate/styrene (PMA/ST), pushed the  $T_o$  (temperature corresponding to the start of degradation) to 285°C when compared with the  $T_o$  of poly(phenyl methacrylate) [PPMA] which was recorded as 190°C [10]. Destabilizing effect of 10 mol % methyl methacrylate (MMA) in allyl methacrylate-methyl methacrylate (AMA-MMA) is apparent as  $T_i$  goes down from 210°C (PAMA) to 200°C for the copolymer [11]. AMA-MMA (blended with aluminum ethoxide—physical mixing of powders) started to degrade at lower temperature than either of monomers, however, stabilization was also observed in different zones of mass-loss [12]. Additive appeared stabilized in the initial stage of thermal decomposition. Similar thermal behavior was observed when PMA-ST system was heated in the presence of aluminum ethoxide [13]. The stabilization went up to 60°C at different points during pyrolysis. When both copolymers, i. e., PMA-ST and AMA-MMA, were mixed with aluminum isopropoxide [9,14], stabilization up to 50°C for the former and 45°C for the latter was clear after initial destabilization. New products were formed as a result of degradation and chemical interaction was proposed. When polymer/copolymer was blended with  $AlBr_3$ ,  $PBr_3$  and  $SnCl_4$  [16-18, 1]—film was cast from common solvent—interesting results were encountered.  $PBr_3$  and  $SnCl_4$  showed stabilization in the presence of the polymer whereas  $AlBr_3$  seemed destabilized. In all these cases, halogen free radicals were generated in the early part of thermal degradation which initiated the decomposition of the polymers. Their interaction produced those compounds which were absent when polymer/copolymer was degraded alone. It is noteworthy that both parts of the additive, i.e., metallic as well as non-metallic played important roles in imparting stability to the blended system.

The present work relates to the thermal degradative studies of copolymer [P(S-co-MMA)] mixed with  $SnCl_4$  (in selected proportions) as a continuation of our previous investigations. The

aim of this investigation was to check the nature of disintegration products comprehensively, i. e., at different temperatures and to propose mechanism based on these evaluations. Thermoanalytical, infrared spectroscopy and Py-GC-MS techniques were utilized to ascertain the interactions or otherwise exhibited by the constituents of current system.

## 2. EXPERIMENTAL

### 2.1 Reagents

All the chemicals used in this research work were of analytical grade. The monomer, methyl methacrylate, was freed from inhibitor (hydroquinone) by first washing it with aqueous 5% sodium hydroxide followed by de-ionized water until neutral and then it was dried over anhydrous calcium chloride for 24 hours [20]. It was distilled under reduced pressure prior to use, only middle portion was selected for polymerization. Styrene (Aldrich) was treated as had already been described [21]. 2, 2'-Azobisisobutyronitrile (AIBN) was chosen as radical initiator for copolymerization and was purified by reported method [22]. The crystals obtained were dried under vacuum and kept in refrigerator (black paper wrapped around bottle). All solvents were distilled by standard procedures before use.

### 2.2 Synthesis of poly(styrene-co-methyl methacrylate)

Styrene (Aldrich) and methyl methacrylate (E. Merck) were purified by the standard procedures. For the production of copolymer the composition of monomers were calculated by using the reported procedure [23-26]. The known quantity of initiator, 2, 2'-azobisisobutyronitrile was taken in the dilatometer and the appropriate amounts of the two monomers were introduced after distillation under vacuum with mild heating. Then dilatometer was sealed under high vacuum after distilling and freezing the whole contents to freezing temperature by liquid nitrogen. The sealed dilatometer was placed in water bath at 60°C for copolymerization to a maximum conversion of 5 per cent for a period of 2 hours. The product was precipitated and reprecipitated from chloroform by methanol and dried under vacuum at room temperature for a couple of days and stored in desiccator. The molecular weight of copolymer was obtained as 120000.

### 2.3 Procedure for the Formulation of Blend

The blends with varying compositions of copolymer and additive in the form of thin films were formulated by using common solvent—acetone—by the known procedure [1].

### 2.4 Pyrolytical Procedure for Copolymer-Additive Blend System

The selected quantity of polymer-additive blend is heated in a special glass assembly under controlled conditions [1]. The products arising as a result of degradation are divided into two parts: the volatile products and final residue. The volatile products which are produced at the degradation temperature are collected in a small tube (immersed in liquid nitrogen) attached to 'U' tube confined in Dewar flask. The fraction produced (which remains liquid at room temperature) is characterized by FTIR and GC-MS techniques in order to establish the nature of compounds. The residue, remaining in the bulb after pyrolysis, is removed and stored in the desiccator for analysis by FTIR spectroscopy to identify the functional groups present in it.

### 2.5 Formulation of Strip for Flammability Test

Pyrex glassware was utilized for dissolving copolymer, additive and copolymer/additive blends. Due to the extremely corrosive nature of additive, it was handled with utmost care. For neat poly (styrene-co-methyl methacrylate) sample, the copolymer was added to sufficient volume of acetone and kept overnight to dissolve it completely. The resultant solution was poured into an aluminum mold with the dimensions: 1 mm × 7 mm × 150 mm (the inside cavity was covered with high density clean polythene sheet). The mold was placed in dark for complete dryness for a period of 48 hrs. In case of blends, copolymer and additive (in definite ratios) were dissolved in acetone separately and placed in cool and dry place for 24 hrs. Individual solutions were then combined and placed in dark place to mix these completely. The content was poured in the mold and allowed to dry for 48 hrs. Dry sample was removed from the mold and placed in the desiccator. The sample was ready for the flammability test [1].

**Table 1. GC-MS results of blend, F4, after heating to high temperature, cooling the contents at room temperature and dissolving in acetone**

Peak No.	Time (min)	MS(m/z) with intensities	Product identified
1.	5.298	78(100)*, 77(30), 51(23), 50(21), 52(19), 39(12)	Benzene
2.	7.393	112 (100), 77 (45), 114 (34), 51 (12), 50 (10), 113 (7)	Chlorobenzene
3.	10.249	138(37), 77(36), 140(12), 103(100), 51(38), 50(17), 140(12), 102(10), 104(9)	1-Chlorostyrene
4.	10.431	146 (100), 148 (64), 111 (36), 75 (20), 150 (10), 113 (9), 50 (8)	1,2-Dichlorobenzene
5.	13.728	118 (100), 117 (64), 103 (45), 78 (28), 77 (18), 91 (16), 115 (14)	$\alpha$ -Methylstyrene
6.	15.86	278 (100), 261 (80), 280 (68), 263 (60), 201 (50), 77 (45), 119 (40), 243 (30), 241 (20), 277 (18), 279 (15), 159 (12), 161 (7)	3-Chloro-3-carboxy-5-methyl-7-phenyl-1,4-octadiene

\*The values given in parenthesis are the relative abundance in %

## 2.6 Instrumentation

Thermoanalytical characterizations were conducted on NETZSCH Simultaneous Thermal Analyzer STA 429. All the measurements were accomplished with 40-60 mg samples (initial mass). Samples were heated over the temperature range from ambient to 800°C in nitrogen (inert atmosphere), using kaolin as reference material. The heating rate was kept as 10°C min<sup>-1</sup>.

Infrared (IR) spectra of additive, copolymer, blend and residues, after heating the blends at different temperatures, were recorded with Nicolet 6700 FTIR spectrometer in the range 4000-400 cm<sup>-1</sup> by directly placing small quantity of samples (solids as well as liquids) on the slit of the spectrometer.

The liquid chromatograph, Hitachi 655-A-11 with GPC software and integrator (D-2200 GPC) along with column GLA-100m (Gelko), was employed for molecular weight determination of copolymer at room temperature. The detector system comprised Hitachi 655-A UV variable wavelength monitor (=254 nm) and SE-51 (Shodex) refractive index detector. Polystyrene standards were used for calibration curves and HPLC grade tetrahydrofuran (Aldrich) was utilized as solvent.

Samples were analyzed by an Agilent 6890N type GC-MS coupled with 5973 inert MSD, Agilent Analytical Instruments, Agilent Technologies, USA. Analysis of the products (mixed in acetone) was performed with a DB-5MS column. The injection volume used in each case was 1  $\mu$ L. Initially the temperature was

raised from 120-150°C at 10°C min<sup>-1</sup> and then from 150-280°C at 15°C min<sup>-1</sup>. The instrument was operated in the electron-impact (EI) mode at 70 eV. The blend, F4 (which was taken as a representative sample for the whole series investigated), was pyrolyzed according to the described procedure. It was heated to high temperature for nearly two minutes and then cooled. Liquid portion was studied by GC-MS. GC is reproduced in Fig. 8 and identified products are given in Table 1.

The horizontal burning test (HBT) of copolymer and its blends was conducted in accordance with the known standard procedures [27].

Blend compositions were formulated by mixing neat copolymer with additive in an aluminum mold with above-quoted dimensions. The specimen was fixed horizontally and a flame (fuelled by natural gas or spirit) was supplied to burn one end of the strip. The time for the flame to reach from the first reference mark on the strip (25 mm from the end) to the second reference mark (at 100 mm from the same end) was measured [28].

## 3. RESULTS AND DISCUSSION

### 3.1 TG-DTG-DTA Characterization

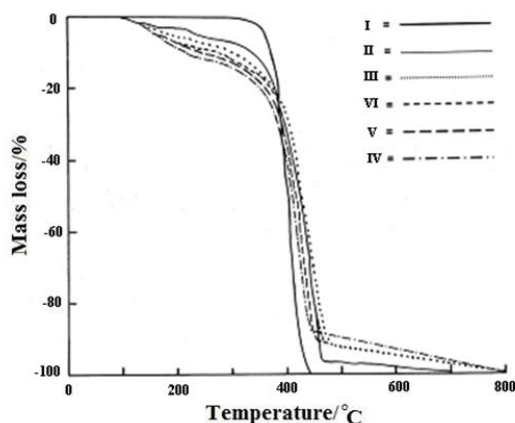
Thermogravimetric curves of copolymer (F) and its blends, F1-F5, are presented in Figs. 1, 2 and 3, whereas TG, DTA and DTG data are summarized in Table 2. The corresponding traces and data of additive have already been reported [1].

Table 2. Thermoanalytical results for copolymer (F) and its blends, F1-F5

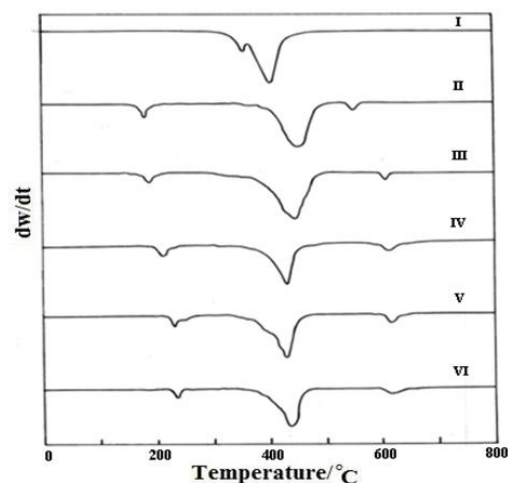
Blends' Code, % (P(S-co-MMA)-SnCl <sub>4</sub> )	Temperature range, °C	Stage	Mass-loss, %	TG, °C				DTG, °C			DTA, °C
				T <sub>0</sub>	T <sub>25</sub>	T <sub>50</sub>	T <sub>max</sub>	I	II	III	Thermal effect
F (100-00)	260-440	I	100	260	380	396	440*	355	406	--	356 (Endo), 418 (Exo)
F1 (97.5-2.5)	90-220	I	4	90	395	420	700	181	448	555	125(Exo), 170(Endo),
	220-460	II	92								260(Endo), 340(Endo), 386
	460-700	III	4								(Endo), 421(Exo)
F2 (95-5)	90-215	I	6	90	390	420	800	190	438	610	130(Exo), 178(Endo),
	215-480	II	86								265(Endo), 345(Endo), 390
	480-800	III	8								(Endo), 425(Exo)
F3 (92.5-7.5)	90-230	I	9	90	385	420	800	210	428	615	132(Exo), 175(Endo),
	230-460	II	82								270(Endo), 350(Endo),
	460-800	III	9								392(Endo), 430 (Exo)
F4 (90-10)	90-240	I	10	90	375	415	800	230	431	618	135(Exo), 180(Endo),
	240-450	II	80								273(Endo), 352(Endo),
	450-800	III	10								395(Endo), 433(Exo)
F5 (87.5-12.5)	90-245	I	12	90	370	420	800	235	435	621	132(Exo), 176(Endo),
	245-440	II	76								269(Endo), 349(Endo), 393
	440-800	III	12								(Endo), 440(Exo)

\* = 100 % mass-loss, Endo = Endothermic, Exo = Exothermic

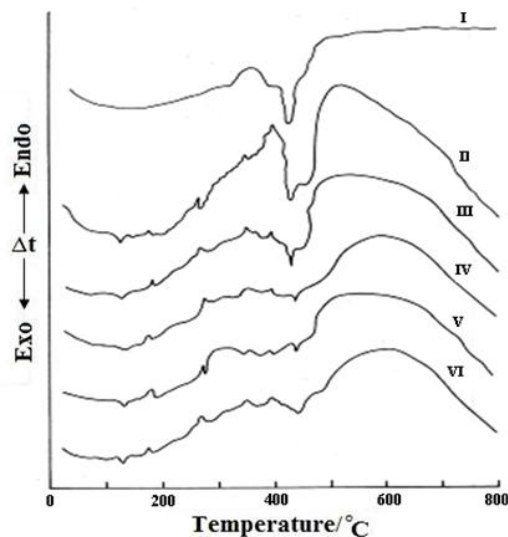
The blend (F1) starts to degrade around 90°C and the first stage comes to an end at 220°C (Fig. 1-II). Four per cent mass-loss is observed. The products evolved at this stage clearly indicate the interaction between the two components of the system. The neat copolymer exhibits  $T_0$  (temperature at which first mass-loss is detected) at 260°C (Fig. 1-I) while additive starts losing mass around 10°C when heated alone. This is another clue for interaction. From 220°C to 460°C, the system goes on degrading (the second stage) as the intermediate is not stable. This intermediate is not pure P(S-co-MMA) as neat polymer commences to decompose around 260°C. So, it is believed that bonds between decomposing  $\text{SnCl}_4$  and P(S-co-MMA) are formed. The second stage which terminates at 460°C accounts for 92% mass-loss. From 220°C to 350°C, only 6% mass-loss out of 92% (for the second stage) requires heating of 130°C, whereas remaining 86% needs temperature of only 110°C, which is indicative of the strength of bonds that developed during the early part of pyrolysis. One DTG peak at 181°C (Fig. 2-II) and two DTA peaks at 125°C and 170°C (Fig. 3-II) are noted for the first stage, on the other hand, one DTG peak at 448°C and four DTA peaks at 260, 340, 386 and 421°C appear for second stage. The sharp fall in TG traces for the second stage manifests the rupture of all types of bonds as the rising energy content cannot be resisted. The third stage starts at 460°C and terminates at 700°C with the mass-loss of 4%. Only one DTG peak at 555°C appears. No residue is noticeable at the completion of degradation process.



**Fig. 1. TG thermograms of P(S-co-MMA)- $\text{SnCl}_4$  blends: F(I), F1(II), F2(III), F3(IV), F4(V) and F5(VI), obtained under dynamic nitrogen atmosphere at heating rate of 10°C/min**



**Fig. 2. DTG thermograms of P(S-co-MMA)- $\text{SnCl}_4$  blends: F(I), F1(II), F2(III), F3(IV), F4(V) and F5(VI), obtained under dynamic nitrogen atmosphere at heating rate of 10°C/min**



**Fig. 3. DTA thermograms of P(S-co-MMA)- $\text{SnCl}_4$  blends: F(I), F1(II), F2(III), F3(IV), F4(V) and F5(VI), obtained under dynamic nitrogen atmosphere at heating rate of 10°C/min**

The second blend of this series, F2, starts losing mass around 90°C and by the end of the first stage (215°C), accounts for 6% mass-loss (Fig. 1-III). It is clear now that by increasing the concentration of additive ( $\text{SnCl}_4$ ),  $T_0$  does not show any change, however, the per cent mass-loss has increased. Same type of interaction is believed to have occurred for this blend as was observed for F1. Second stage (215-480°C)

gives a mass-loss of 86%. From 215°C to 350°C, the mass-loss is only 10% which is regarded as resistance offered by the bonds/interactions developed in the earlier part of the degradation between the components of the system. For first stage, one DTG peak at 190°C (Fig. 2-III) and two DTA peaks at 130°C and 178°C appear (Fig. 3-III). For second step, one DTG and four DTA peaks are noticed at 438, 265, 345, 390 and 425°C, respectively. Third stage starts at 480°C and terminates at 800°C with a mass-loss of 8%. One DTG peak at 610°C supports the result of TG. No residue is found at the termination of the degradation process.

The blend, F3, begins to degrade around 90°C and loses 9% of original mass in the first stage which terminates at 230°C (Fig. 1-IV). The intermediate formed at this stage is not stable, so pyrolysis continues and the second step shows a mass-loss of 82% in the temperature range of 230-460°C. One DTG and two DTA peaks appear for first stage at 210, 132 and 175°C, respectively, however, for second stage one DTG and four DTA peaks at 428, 270, 350, 392 and 430°C, respectively, arise (Figs. 2-IV and 3-IV, respectively). From 230°C to 350°C, only 10% mass-loss is observed which is indicative of the strength of bonds that developed during the early part of pyrolysis. Third stage commences at 460°C and ends at 800°C with a mass-loss of 9%. One DTG peak at 615°C supports the result of TG. No residue is found at the termination of the degradation process.

A mass-loss of 10% is exhibited by F4 for first stage. It begins to decompose around 90°C and stops losing mass around 240°C (Fig. 1-V). One DTG (Fig. 2-V) and two DTA peaks (Fig. 3-V) are found at 230, 135 and 180°C, respectively. The intermediate does not remain stable at 240°C. The second step comes to an end at 450°C marking a mass-loss of 80%. The first 10% mass-loss of second stage requires heating of 90°C in the temperature range, 240-350°C, which is attributed to the resistance offered by strong bonds/links produced during the early part of the pyrolysis. One DTG and four DTA peaks are observed for second stage at 431, 273, 352, 395 and 433°C, respectively. The third stage begins at 450°C and ends at 800°C with a mass-loss of 10%. One DTG peak is observed at 618°C. No residue is noticeable at the completion of degradation process.

F5 starts its mass-loss around 90°C for first stage which comes to an end at 245°C. One DTG and two DTA peaks arise for this step at

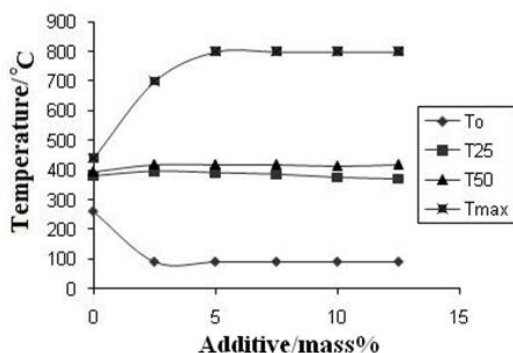
235°C, 132°C and 176°C, respectively. Twelve per cent mass-loss is evident from TG traces (Fig. 1-VI). The intermediate that is not stable up to 245°C, commences disintegrating as the energy content increases. The second stage terminates at 440°C with a mass-loss of 76%. One DTG and four DTA peaks are found (Figs. 2-VI and 3-VI, respectively) at 435, 269, 349, 393 and 440°C, respectively. The first 10% mass-loss for the second step (out of 76%) requires heating of 105°C (from 245 to 350°C) whereas the remaining larger portion (66%) leaves the scene for a heating of 90°C (350-440°C). This is attributed to the strength of the bonds present in the intermediate. The third stage starts at 440°C and ends at 800°C with a mass-loss of 12%. One DTG peak at 621°C is observed to support the TG trace. There was no residue at the end of pyrolysis for this blend.

It is inferred that the interaction is clear between the components of the system throughout the series, i.e., F1-F5.  $T_o$  value and the nature of interaction is same for all members of the series. Mass-loss for the first stage goes on increasing as the percentage of additive is increased in the blend, F1 to F5. The percentage of degradation for first stage is higher than the total percentage of additive in the blends, i.e., F1-F3. Molecular-level mixing of the constituents favors the development of links between them which, in turn, gives way to early degradation of both parts. The evolution of new product in the early part of pyrolysis confirms the chemical interaction and mutual influence of the ingredients on each other's decomposition.

### 3.2 Influence of Blends' Composition on Thermal Behavior

A trend of destabilization is encountered (Fig. 4) when  $T_o$  (temperature at which first mass-loss is detected) is pursued for copolymer and its blends' degradation. No further destabilization is observed with the increase of additive's percentage. Almost similar trend of stabilization is noted for all the blends which is independent of additive's concentration. It may be argued that a number of links are developed between  $S_n$  and pendent oxygens of copolymer per unit volume of additive and this is independent of the concentration of additive. For  $T_{25}$  (temperature for 25% mass-loss), a slight stabilization of 5 to 10°C is noticed as the concentration of additive is increased, which may be ascribed to the number of links created between copolymer and degraded additive. However, with further

increase in additive's concentration in blends, inappreciable destabilization of the blended system becomes evident. This seems to be due to the production of free radicals ( $Cl^{\bullet}$ ) from the degradation of additive in this region, which hastens early degradation of copolymer. At  $T_{50}$  (temperature at which 50% mass-loss is noticed), a very appreciable stabilization of 25°C is observed with varying additive percentage as high energy content is resisted by a variety of interactions or bonds between the constituents of the system.  $T_{max}$  (temperature for maximum mass-loss) is lower for copolymer when compared with its blends, which is a clear indication that either metal from additive develops very strong bonds with the disintegrating copolymer or gives rise to such compounds that decompose only at higher temperature. This trend shows an increased stabilization of the blends as the percentage of additive is enhanced.



**Fig. 4.** Influence of blends' composition on T0, T25, T50 and Tmax values of copolymer (F) and blends (F1-F5)

### 3.3 Infrared Spectroscopic Measurements

#### 3.3.1 Copolymer

The peak for ester group of MMA is observed at  $1725\text{ cm}^{-1}$  (Fig. 5-I). Presence of styrene in close proximity may have caused the slight shift noticed in the preceding stretching. Bands in the regions,  $3000\text{-}2940\text{ cm}^{-1}$  and  $3040\text{-}3010\text{ cm}^{-1}$ , are assigned to aliphatic and aromatic C-H stretchings, respectively. For these, overtones appear in the region  $2000\text{-}1660\text{ cm}^{-1}$ . Aromatic C=C stretchings are found at  $1606$ ,  $1495$  and  $1460\text{ cm}^{-1}$ . As peaks in the region  $1640\text{-}1630\text{ cm}^{-1}$  are absent, it is believed that copolymerization has taken place [29-32].

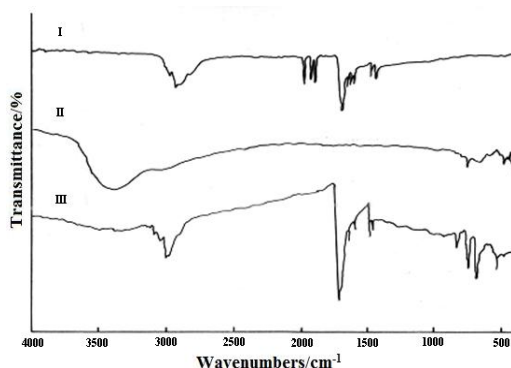
#### 3.3.2 Additive

A broad band at  $3394\text{ cm}^{-1}$  is assigned (Fig. 5-II) to the presence of water. Moisture absorbance by  $\text{SnCl}_4$  could not be prevented despite all precautions. Typical peaks at  $769$ ,  $505$ , and  $406\text{ cm}^{-1}$  are believed to have arisen from Sn-Cl bonds.

#### 3.3.3 Blend

The IR of the blend, F4 ( $\text{P(S-co-MMA)} + \text{SnCl}_4$ ), lacks broad band at  $3394\text{ cm}^{-1}$  for water. This is a clear manifestation that the additive has co-ordinated comprehensively with the copolymer (in all terms with MMA units) and, thus, not available as a 'free' and separate entity. This obviates absorption of water from surroundings.

The peaks for C-H stretchings (aliphatic and aromatic) are present in their normal region, i.e.,  $3040\text{-}2940\text{ cm}^{-1}$  (Fig. 5-III). The bands for ester linkage are now found around  $1721\text{-}1695\text{ cm}^{-1}$  clearly indicating the 'co-ordination' of  $\text{SnCl}_4$  with carbonyl oxygen. The usual carbonyl stretching frequency for MMA units appears around  $1735\text{-}1730\text{ cm}^{-1}$ . Sn-Cl bonds also show some shifting as Sn is involved in co-ordination and chlorines are being 'attracted' by methyls attached to backbone carbons and phenyls of the styrene units. These are now shown at  $757$ ,  $519$ , and  $420\text{ cm}^{-1}$ . The C=C (aromatic) stretchings appear displaced as these are found at  $1603$ ,  $1490$  and  $1450\text{ cm}^{-1}$  which may be regarded as the effect of surroundings. The bands in the region  $560\text{-}830\text{ cm}^{-1}$  may be assigned to the 'link' between chlorine of additive and methyls and phenyls attached to carbon backbone.



**Fig. 5.** The IR spectra of neat copolymer, F(I), Additive(II) and blend, F4(III)



### 3.4 IR of Blend Heated at Different Temperatures

The blend was heated at three temperatures, viz., 250, 350 and 450°C to get more information on the pattern of the degradation process. Monitoring of the pyrolytical course of the blend is expected to improve understanding of decomposition mechanism. These temperatures were selected to check the mode of interaction of the blended material in the second stage of degradation or close to the start of third stage of disintegration (TG curves).

When heated to 250°C (it was cooled to room temperature and IR of liquid portion was recorded), the IR (Fig. 6-I) showed peaks around 3110-2940  $\text{cm}^{-1}$  for C-H stretchings (aliphatic as well as aromatic). The intensities are low and the sizes diminished. This may be attributed to the evaporation of low boiling products including  $\text{H}_3\text{C-Cl}$ . The bands which show the coordination of Sn with C=O are shifted to lower frequencies (1716-1690  $\text{cm}^{-1}$ ). It is also noticed that size and intensity of these peaks have decreased. This may be attributed to the decrease in MMA units either due to their degradation or the formation of new bonds with Sn. It is pertinent to note that the amount of MMA units per unit volume of additive is much less as compared to the blends of PMMA and  $\text{SnCl}_4$  [1]. Bands for the existence of anhydride rings are present (1803, 1759, 1026  $\text{cm}^{-1}$ ), however, broad peak for water (3394  $\text{cm}^{-1}$ ) is absent. Water is thought to have evaporated immediately after its production. Small sizes of the peaks for anhydride rings are an indication that very small number of such rings is formed at this temperature. There is no peak around 1190  $\text{cm}^{-1}$  which may be assigned to the absence of Sn-C bond. For C=C (aromatic) stretchings, peaks with diminished sizes appear around 1600, 1497 and 1456  $\text{cm}^{-1}$ . Compounds involving benzene ring (chlorobenzene, dichlorobenzene, etc.) would have evaporated by this temperature which may be the reason of reduced peak sizes for C=C (aromatic) stretchings. Sn-Cl peaks spring around 755, 511 and 415  $\text{cm}^{-1}$ .

Upon heating the blend to 350°C (second stage of degradation-TG curves), the IR (Fig. 6-II) of the liquid portion revealed the presence of C-H stretchings in the region 3110-2940  $\text{cm}^{-1}$  (both aliphatic and aromatic) with comparatively reduced sizes and intensity (reduction observed when compared with IR taken at 250°C). Same decrease for co-ordination of Sn with C=O seems to have occurred when IR at two

temperatures are compared, i.e., 250 and 350°C. For C=C (aromatic) stretchings, bands are noticeable at 1600, 1500 and 1455  $\text{cm}^{-1}$ . The amount of anhydride rings has further gone down (1800, 1760, 1030  $\text{cm}^{-1}$ ). Water, understandably so, is absent (broad peak at 3394  $\text{cm}^{-1}$ ). A peak has appeared at 1190  $\text{cm}^{-1}$  hinting at the presence of Sn-C, however, no compound involving this bond could be detected in GC-MS investigations. Sn-Cl stretchings appear at the normal positions, i.e., 753, 509 and 412  $\text{cm}^{-1}$ .

Heating the blend to 450°C and then cooling the remaining contents to room temperature shed more light on the nature of products present at this temperature. The IR (Fig. 6-III) reveals that C-H stretchings for aliphatic and aromatic fragments are still noticeable, though with reduced intensity and size when compared with the C-H stretchings of the blend heated at 350°C. The diminished intensity of C=O stretchings may be attributed to the formation of Sn-O-C type bonds (peaks in the region 1200-900  $\text{cm}^{-1}$ ) since the current temperature is very close to either the completion of second stage of degradation or the start of third stage, i.e., formation of residue (TG traces). No anhydride rings are present as the characteristic peaks for these rings are absent. Few Sn-Cl bonds are believed to exist even at this temperature (bands at 765, 509 and 410  $\text{cm}^{-1}$ ). The disappearance of peak at 1190  $\text{cm}^{-1}$  indicates the absence of any compound with Sn-C bond. Very few peaks signifying the presence of aromatic C=C bond are found around 1600-1450  $\text{cm}^{-1}$ . The appearance of non-aromatic unsaturation (peak in the region 1630-1620  $\text{cm}^{-1}$ ) suggests that some segments are present which have developed unsaturation at this temperature (fragments with limited chain length). The bands for C-Cl stretching are also observed (830-560  $\text{cm}^{-1}$ ) which may be linked to the attachment of Cl with undegraded carbon backbone.

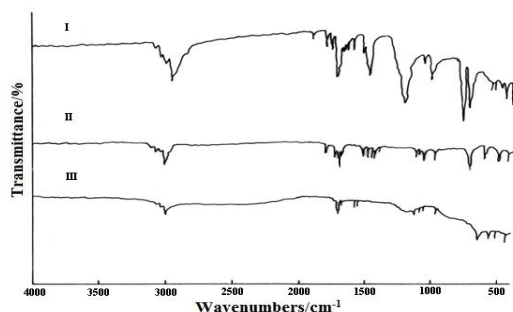


Fig. 6. IR spectra of blend, F4, after heated at 250°C (I), 350°C (II) and 450°C (III)

### 3.5 IR of Residue after Pyrolysis

The IR of residue (Fig. 7-II) is very simple with very few peaks. Bands in the region  $3000\text{-}2922\text{ cm}^{-1}$  are assigned to C-H stretchings of aliphatic nature. The peaks found around  $1710\text{-}1697\text{ cm}^{-1}$  points towards the existence of coordinated structure. For Sn-O-C bonds, the stretchings may be observed in the region  $1200\text{-}900\text{ cm}^{-1}$ . The bands for Sn-Cl ( $765$ ,  $509$  and  $410\text{ cm}^{-1}$ ) stretchings are absent indicating complete involvement of Sn with undegraded part of copolymer via oxygen resulting in char. It can be concluded that residue consists of char and metallic Sn (visual inspection was also carried out).

### 3.6 IR of Blend Heated at High Temperature

This was carried out to have an overall glimpse of the mode of degradation and the nature of products. Blend was heated at high temperature for a couple of minutes, cooled and liquid portion was subjected to IR (Fig. 7-I).

Peaks for aliphatic and aromatic C-H stretchings are noticeable at their normal positions ( $3000\text{-}2940\text{ cm}^{-1}$  and  $3040\text{-}3010\text{ cm}^{-1}$ , respectively). Co-ordination is evident as before ( $1715\text{-}1695\text{ cm}^{-1}$ ) [33,34], however, a small peak at  $1732\text{ cm}^{-1}$  suggests that a few C=O are not involved in the co-ordination process (presence of styrene units among MMA 'blocks' may be the reason). It seems a rare situation as in none of the IRs taken at other temperatures (at  $250$ ,  $350$  and  $450^\circ\text{C}$ ) exhibited 'free' C=O; even the blend's IR was devoid of this stretching. Bands at  $1803$ ,  $1758$  and  $1026\text{ cm}^{-1}$  (anhydride rings), at  $1600$ ,  $1500$  and  $1457\text{ cm}^{-1}$  (C=C stretchings for aromatic moieties), around  $830\text{-}560\text{ cm}^{-1}$  (C-Cl) and at  $767$ ,  $511$  and  $409\text{ cm}^{-1}$  (Sn-Cl) confirm the presence of functionalities that have already been observed where the blend was heated to  $250$ ,  $350$  and  $450^\circ\text{C}$  and IRs were recorded of liquids, thus obtained, at these temperatures. GC-MS results lend support to current findings.

### 3.7 Pyrolysis-gas Chromatography-mass Spectrometry Characterization

GC-MS is presented in Fig. 8 and the products identified are contained in Table 1. The first peak is recognized as benzene. This compound also appears if the copolymer is pyrolyzed neat, however, its increased amount points to the

involvement of additive as suggested in Schemes 2 and 4. Despite finding less number of styrene units per unit chain length of blend, the higher concentrations of benzene substantiate the notion of interaction between copolymer and blend during thermal degradation.

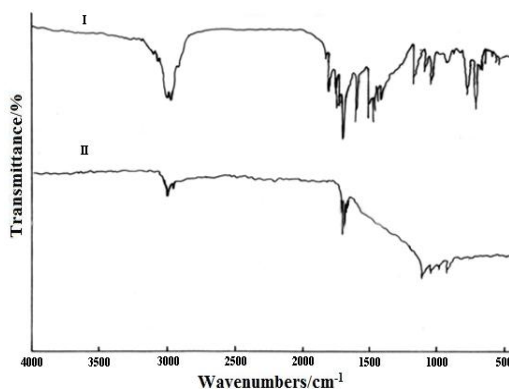


Fig. 7. IR spectra of blend, F4, after pyrolysis at high temperature—liquid (I) and residue (II)

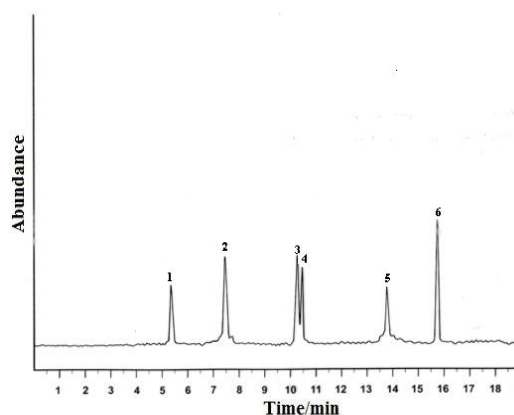


Fig. 8. GC-MS results of blend, F4, heated to boiling, cooled and dissolved in acetone

Second peak gives the indication of chlorobenzene. As it is not the degradation product of neat copolymer, its presence clearly shows the influence of additive on the production of this substance. Scheme 1 gives the proposed mechanism for the formation. Two free radicals (chlorine and benzene) combine to yield chlorobenzene.  $\text{SnCl}_4$  provides  $\text{Cl}^\bullet$ .

For the third peak, 1-chlorostyrene is identified (Scheme 2). The production route seems to first pass through the splitting of  $^\bullet\text{OCOCH}_3$  from the methyl methacrylate unit and, secondly, the formation of bond between phenyl (free radical)

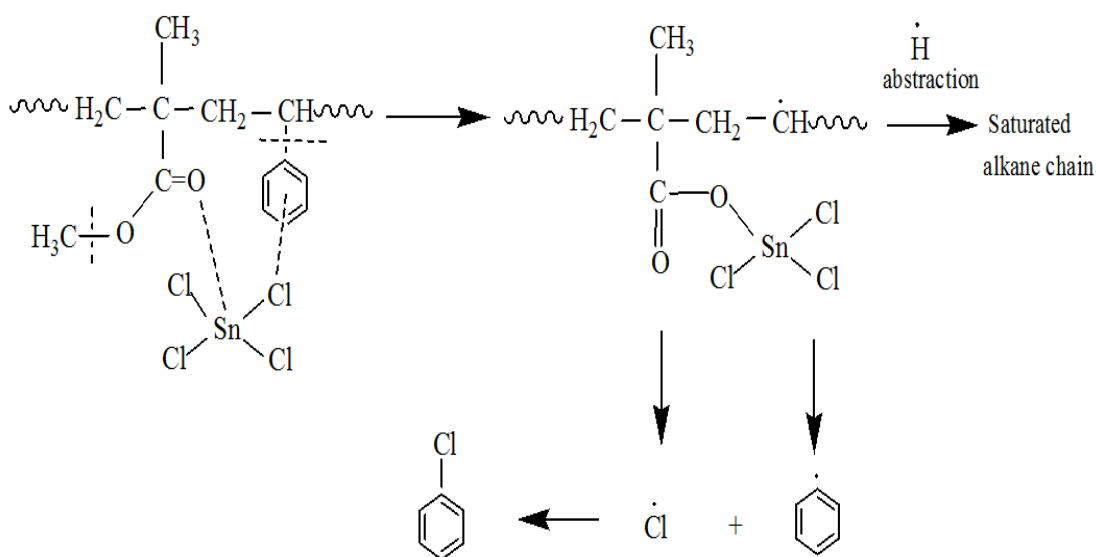
and that part of main chain from where the former breakage occurred. Thereafter, the degradation proceeds along the main chain resulting in 1-methylstyrene. Subsequent replacement of methyl with chlorine affords 1-chlorostyrene. Peak four hints at the fragmentation pattern (mass spectrum) of 1, 2-dichlorobenzene. This appears to have arisen due to the reaction between two degradation products, i.e., 1-chlorobenzene and  $\text{Cl}^\bullet$ . This compound also implies that the time span for the disappearance of the two degradation products from the scene is quite long. This production sheds light on the fact that not only chlorine (free radicals) is released in the beginning but also in the later part of the pyrolytical process.

On peak five, the compound identified is  $\alpha$ -methyl styrene. A part of it gets converted into 1-chlorostyrene (Scheme 2). It may be due to consumption of chlorine free radicals by other reactions, for instance, conversion of benzene to 1-chlorobenzene (Scheme 1) and emergence of 1, 2-dichlorobenzene (Scheme 3).

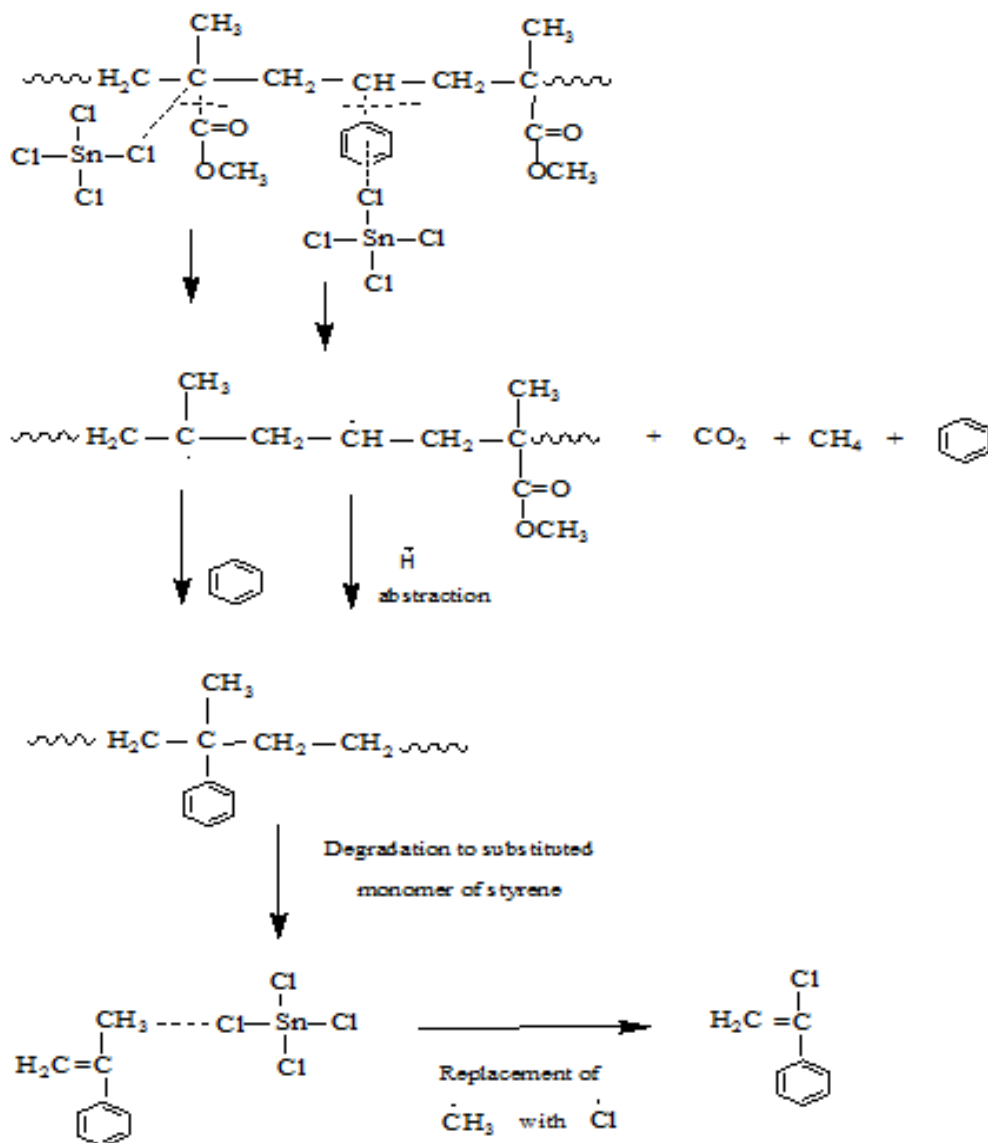
The last peak (no. 6) reveals the presence of a large molecule, i. e., 3-chloro-3-carboxy-5-methyl-7-phenyl-1, 4-octadiene (Scheme 4). Its formation is the result of interaction between the constituents of blends. As the chlorine and the acidic entity are the parts of this molecule, some modifications must have clearly been effected by

the additive on the copolymer. Absence of oligomers of styrene and monomers of methyl methacrylate may be attributed to the role of additive which "disrupts" the normal thermal degradation pattern of the copolymer, i. e., the styrene units are "unable" to exert disproportionate stabilizing effect on the methyl methacrylate polymer chain despite: (1) the presence of fewer unstable chain ends in copolymers than PMMA because of a favored cross-termination step in the copolymerization; and (2) the operative 'cage effect' (advanced by McNeill) results in the production of a pair of polystyryl radicals after an initial scission between a pair of MMA units in the copolymer chain, thus, preventing further unzipping (this indicates that thermograms for P(S-co-MMA) are not simply an 'average' of the thermograms for the corresponding homopolymers [35-42]. The additive can "bind" (physical interaction) the pendent groups of the co-monomer units simultaneously along with main chain.

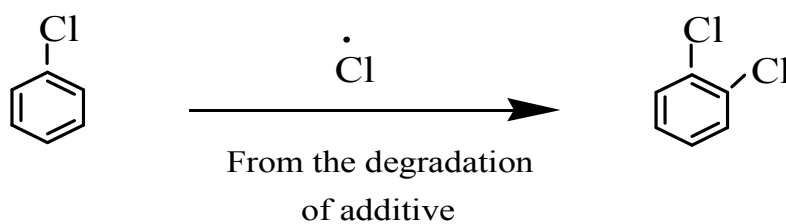
The "cyclic" structure obtained in this way, may impart stability to the degrading copolymer. Chemical interaction, based on the formation of bonds between the additive and copolymer chains, may also strengthen the framework of the blend, apart from producing new compounds [43,44].



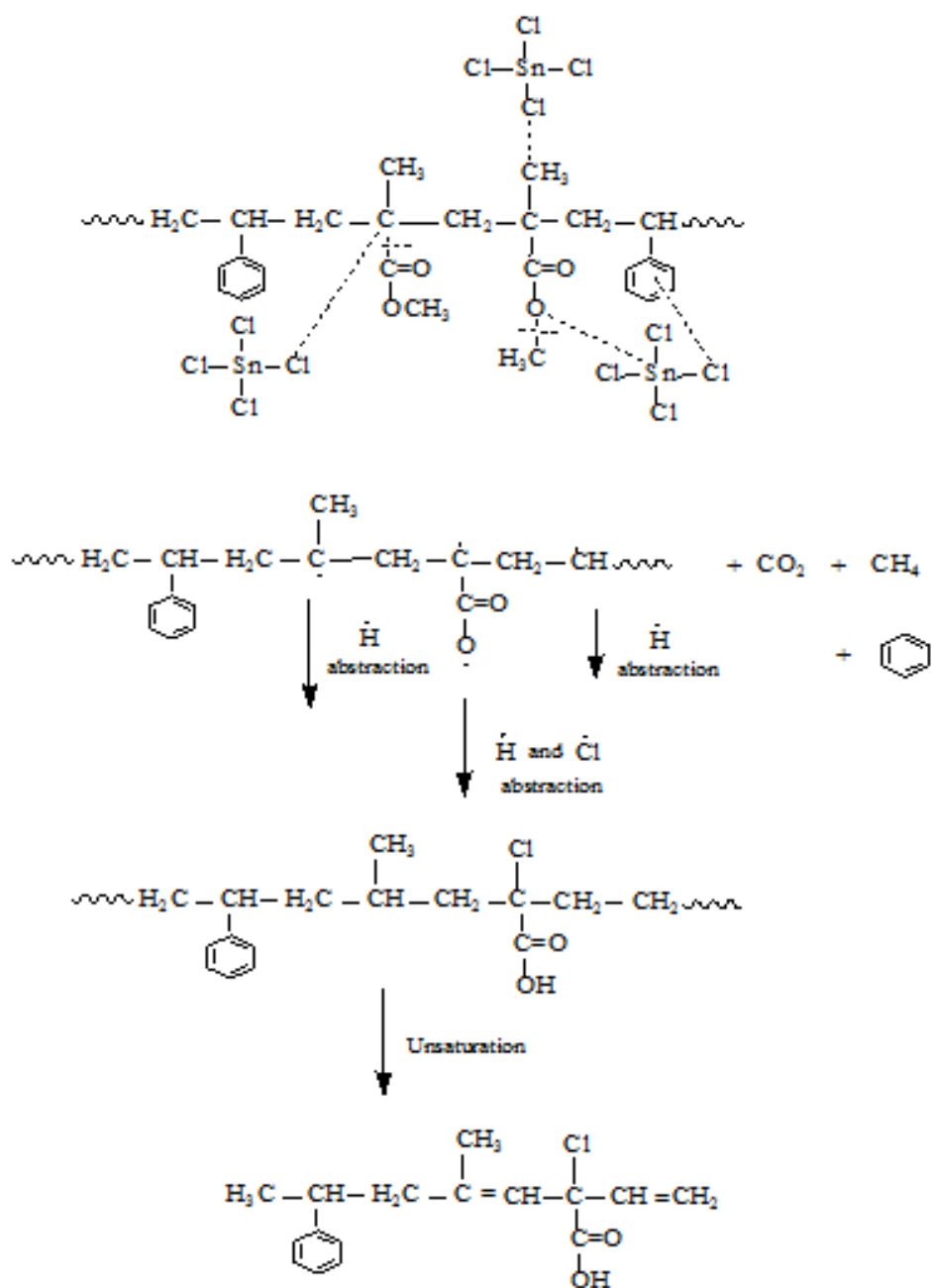
**Scheme 1. Pathway to chlorobenzene**



Scheme 2. Arising of  $\alpha$ -methylstyrene and 1-chlorostyrene



Scheme 3. Formation of 1,2-dichlorobenzene



Scheme 4. Production of a large molecule with multiple functionalities

Table 3. Horizontal burning rate for neat copolymer (F) and P(S-co-MMA)-SnCl4 blends (F1-F5)

Copolymer/blend code number	F	F1	F2	F3	F4	F5
Time to burn (sec)	22	48	58	70	86	101
Length of strip (mm)	75	75	75	75	75	75
HBR (mm/sec)	3.4	1.56	1.29	1.07	0.87	0.74

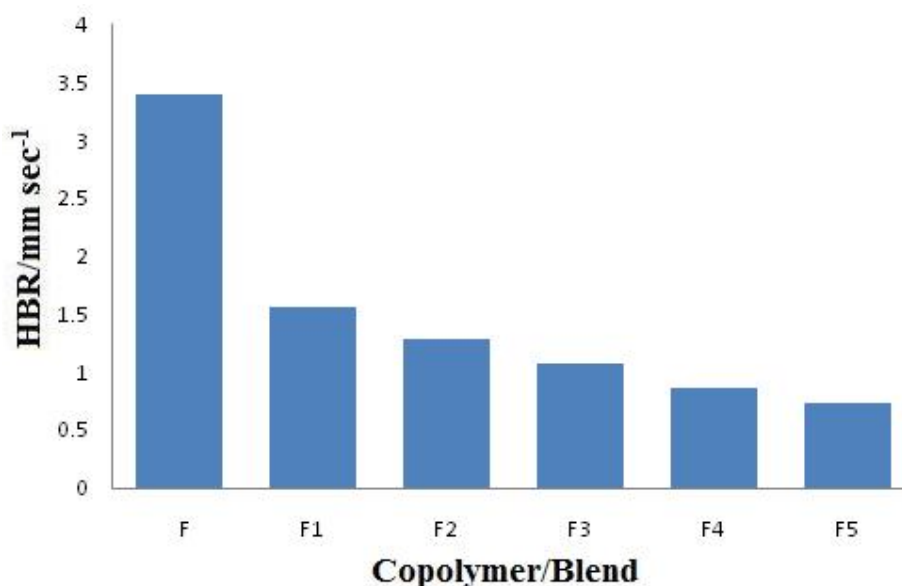


Fig. 9. Horizontal burning rate of copolymer (F) and its blends, F1-F5

### 3.8 Flammability of Copolymer and Blends

The results of HBR for neat copolymer and its blends, F1 to F5, are reproduced in Table 3. It is observed that the burning rate of blend (F1), with lowest percentage of additive (2.5%), is three times less than the neat copolymer (D), whereas with 12.5% additive, 5 times decrease in burning rate is noted (Fig. 9). This unfolds the effectiveness of additive regarding flame retardance. A linear trend of HBR is obtained which indicates that higher the concentration of additive in the blend, lower is the burning rate; this also confirms the homogeneous spread of additive in the copolymer. A convincing clue is, thus, furnished by this parameter for the interaction of additive with the studied copolymer at molecular level.

### 4. CONCLUSION

- I. Neat copolymer degrades in two stages whereas blends and additive in three. Residue is observed only in the pyrolysis of additive.
- II. The low-temperature degradation of the blend is thought to occur due to the decomposition of additive releasing chlorine free radicals.
- III. On comparing  $T_o$ 's (temperature at which first mass-loss is detected) of blends and additives, it can be observed that additive

shows stabilization in the presence of copolymer.

- IV. When  $T_o$ 's of blends is compared, it is inferred that early destabilization of the copolymer is independent of additive's concentration, i.e., as the concentration of the additive is enhanced from 2.5% to 12.5%, no change in  $T_o$  is noted.
- V.  $T_{max}$  for blends does not alter if concentration of additive varies from 5% to 12.5%.
- VI. Various products were identified which were attributed to the interaction of blended constituents, e. g., benzene, chlorobenzene, chlorostyrene, 1,2-dichlorobenzene and a large molecule with many functional groups. Benzene may be regarded as either the degradation product of co-monomer unit, i. e., styrene or the outcome of additive's influence on the same unit.
- VII. The early disintegration of additive furnishes chlorine free radicals which, in turn, attack the degrading copolymer forming entirely different compounds (not found when copolymer and additive are pyrolyzed alone). In one of the compounds, chlorine appears to have replaced  $-CH_3$  group on a short chain.
- VIII. Neat polystyrene, when pyrolyzed, renders oligomers. In present investigation, styrene units did not show the usual thermal behavior clearly suggesting the influence

of additive and co-monomer unit (MMA) on its decomposition. It is understandable as the number of styrene units per chain of copolymer is low and frequency of chain transfer reactions becomes less likely due to the presence of other components in the system.

- IX. In the last stage of degradation, the breakage of Sn-O-C bonds is associated with higher energy. The number of such bonds is less as the number of MMA units per chain of the copolymer is low [in comparison with (PMMA)]. As the temperature rises, the degradation products leave the scene slowly.

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### COMPETING INTERESTS

Author has declared that no competing interests exist.

### REFERENCES

1. Arshad M, Masud K, Arif M, Rehman S, Saeed A, Zaidi JH. Characterization of poly (methyl methacrylate)-tin (IV) chloride blend by TG-DTG-DTA, IR and Pyrolysis-GC-MS techniques. Bull. Korean Chem. Soc. 2011;32(9):3295-3305.
2. Ahmed J, Zhang JX, Song Z, Varshney SK. Thermal properties of polyactides: Effect of molecular mass and nature of lactide isomer. J. Therm. Anal. Calorim. 2009;95(3):957-64.
3. Worzakowska M. The influence of chemical modification of unsaturated polyesters on viscoelastic properties and thermal behavior of styrene copolymers. J. Therm. Anal. Calorim. 2009;96(1):235-41.
4. Aboulkas A, Harfi KE, Bouadili AE, Nadifiyine M, Benchanaa M. Study on the pyrolysis of moroccan oil shale with poly (ethylene terephthalate). J. Therm. Anal. Calorim. 2009;96(3):883-90.
5. Szocik H, Jantas R. Multimonomer and cross-linked polymers formed by its copolymerization—Thermal studies. J. Therm. Anal. Calorim. 2004;76(1):307-12.
6. Chen H, Hu X, Cebe P. Thermal properties and phase transitions in blends of Nylon-6 with silk fibroin. J. Therm. Anal. Calorim. 2008;93(1):201-6.
7. Grassie N, McNeill IC, Cooke I. Thermal degradation of polymer mixtures. I. degradation of polystyrene-poly (methyl methacrylate) mixtures and a comparison with the degradation of styrene-methyl methacrylate copolymers. J. Appl. Polym. Sci. 1968;12:831-37.
8. Gentilhomme A, Cochez M, Ferriol M, Oget N, Mielozynski JL. Thermal degradation of methyl methacrylate polymers functionalized by phosphorus-containing molecules-II: Initial flame retardance and mechanistic studies. Polym. Degrad. Stab. 2003;82:347-55. and references therein.
9. Zulfiqar S, Masud K, Ameer Q. Thermal degradation behavior of blends of phenyl methacrylate-styrene copolymers with aluminum isopropoxide. J. Therm. Anal. Calorim. 2003;73(3):877-86.
10. Zulfiqar S, Masud K, Siddique B, Piracha A. Thermal degradation of phenyl methacrylate-styrene copolymers. Polym. Degrad. Stab. 1996;52(3):293-99.
11. Zulfiqar S, Masud K, Piracha A, McNeill IC. Thermal degradation of allyl methacrylate-methyl methacrylate copolymers. Polym. Degrad. Stab. 1997;55(3):257-63.
12. Zulfiqar S, Masud K. Thermal degradation of blends of allyl methacrylate-methyl methacrylate copolymers with aluminum ethoxide. Polym. Degrad. Stab. 2000; 70(2):229-36.
13. Zulfiqar S, Masud K, Ameer Q. Thermal degradation of blends of phenyl methacrylate-styrene copolymers with aluminum ethoxide. Polym. Degrad. Stab. 2002;77(3):457-64.
14. Zulfiqar S, Masud K. Thermal degradation of blends of allyl methacrylate-methyl methacrylate copolymers with aluminum isopropoxide. Polym. Degrad. Stab. 2002; 78(2):305-13.
15. Arshad M, Masud K, Arif M, Rehman S, Chohan ZH, Arif M, Qureshi AH, Saeed A, Salma U, Awan MS. A comparative study of roles played by aluminum tribromide and aluminum acetylacetonate on the thermal degradation of PMMA by simultaneous



- thermoanalytical techniques. *The Nucleus*. 2008;45(1-2):63-72.
16. Arshad M, Masud K, Arif M, Rehman S, Arif M, Zaidi JH, Chohan ZH, Saeed A, Qureshi AH. The effect of  $\text{AlBr}_3$  additive on the thermal degradation of PMMA: A study using TG-DTA-DTG, IR and Py-GC-MS techniques. *J. Therm. Anal. Calorim.* 2009; 96:873-81.
  17. Arshad M, Masud K, Arif M, Rehman S, Zaidi JH, Arif M, Saeed A, Yasin T. The thermoanalytical, infrared and pyrolysis-gas chromatography-mass spectrometric sifting of poly (methyl methacrylate) in the presence of phosphorus tribromide. *Nat. Sci.* 2010;2(4):307-319.
  18. Arshad M, Masud K, Arif M, Saeed A. Mechanistic study of thermal behavior of poly (vinyl acetate) blended with aluminum tribromide: An investigation aided by IR and Py-GC-MS techniques. *J. Therm. Anal. Calorim.* 2014;115:759-769.
  19. Arshad M, Masud K, Saeed A.  $\text{AlBr}_3$  impact on the thermal degradation of P(S-co-MMA): A study performed by contemporary techniques. *Iranian Poly. J.* 2012;21(3):143-155.
  20. Riddick JA, Bunger WB, Sakano TK. *Organic solvents-physical properties and methods of purification*. New York, John-Wiley and Sons; 1986.
  21. Priddy DB, Pirc M. Purification of styrene for anionic polymerization. *J. Appl. Polym. Sci.* 1990;40(1-2):41-45.
  22. Seymour RB, Carraher Jr CM. *Polymer Chemistry, An introduction*, 2nd edn, New York, Marcel Dekker Inc; 1988.
  23. Meyer VE. Reactivity ratios of styrene and methyl methacrylate at 90°C. *J. Polym. Sci. Part A1, Polym. Chem.* 1967;5(6):1289-96.
  24. Cabaness WR, Lin TYC, Parkanyi C. Effect of pH on the reactivity ratios in the copolymerization of acrylic acid and acrylamide. *J. Polym. Sci. Part A-1, Polym. Chem.* 1971;9(8):2155-70.
  25. Lewis FM, Walling C, Cummings W, Briggs ER, Mayo FR. Copolymerization, IV: effects of temperature and solvents on monomer reactivity ratios. *J. Am. Chem. Soc.* 1948;70:1519-23.
  26. Nozaki N. Reactivity of monomers in copolymerization. *J. Polym. Sci.* 1946; 1(16):455-65.
  27. Flammability Test, ASTM, D 635-14.
  28. Sain M, Park SH, Suhara F, Law S. Flame retardant and mechanical properties of natural fibre-PP composites containing magnesium hydroxide. *Polym. Degrad. Stab.* 2004;83:363-67.
  29. Smith AL. *Applied infrared spectroscopy fundamentals, techniques and analytical problem-solving*, New York, John Wiley and Sons, A Wiley-Interscience Publication. 1979;308:297.
  30. *The Sadtler Standard Spectra*, Philadelphia PA 5, Sadtler Research Laboratories; 1974.
  31. Robinson JW, editor. *CRC handbook of spectroscopy*, USA, CRC Press Inc. 1974; 2.
  32. Szymanski HA, Erikson RE, editors. *Infrared band handbook*, 2<sup>nd</sup> edn. New York, IFI/Plenum. 1970; 1 and 2.
  33. Chandrasiri JA, Wilkie CA. Thermal degradation of poly (methyl methacrylate) in the presence of tin (IV) chloride and tetraphenyltin. *Polym. Degrad. Stabili.* 1994;45(1):91-96.
  34. Chandrasiri JA, Wilkie CA. The thermolysis of poly (methyl methacrylate) in the presence of phenyltin chlorides  $\text{Ph}_4\text{SnCl}_{4-x}$  ( $x=1-3$ ). *Polym. Degrad. Stabili.* 1994; 45(1):83-89.
  35. Hurduc N, Cascaval CN, Schneider IA, Reiss O. Etude de la degradation thermique de copolymers: Comparaison de melanges de polymers, decopolymers sequences, statistiques et alternes a bas de styrene et al de methacrylate de methyl. *Europ. Polym. J.* 1975;11:429-435.
  36. McNeill IC. A study of the degradation of methyl methacrylate polymers and copolymers by thermal volatilization analysis. *Euro. Polym. J.* 1968;4:21-30.
  37. Grassie N, Farish E. The thermal degradation of copolymers of styrene and methyl methacrylate. *Euro. Polym. J.* 1976; 3:305-315. and references therein.
  38. Grassie N, Grant EM. The thermal degradation of copolymer of  $\alpha$ -chloroacrylonitrile with styrene and methyl methacrylate. *Euro. Polym. J.* 1966;2:255-268.
  39. Gronowski A, Wojtezak Z. Thermal stabilities of copolymers of styrene with lithium, sodium and potassium acrylates and methacrylates. *Acta polymerica.* 2003; 40(4):265-268.
  40. Cascaval CN, Schneider IA, Poinescu IGC, Butnaru M. Pyrolysis-gas



- chromatography of some copolymers of styrene. Euro. Polym. J. 1979;15:661-666.
41. Beldie C, Onu A, Bourceanu G, Poinescu IGC. Glass transition temperatures of some copolymers of styrene with methyl methacrylate using DTA and chromatographic data. Euro. Polym. J. 1985;2(3):321-323.
42. Hamoudi A, McNeill IC. Preparation and degradation of copolymers of methyl methacrylate with alkali metal methacrylates-III: quantitative studies of products of degradation to 500°C. Euro. Polym. J. 1978;14:779-784.
43. Tsuge S, Ohtani H, Watanabe C. Pyrolysis-GC/MS data book of synthetic polymers: Pyrograms, Thermograms and MS of Pyrolyzates, 1<sup>st</sup> edn. Amsterdam, Netherland, Elsevier; 2011.
44. Wilkie CA, Utracki LA, (Editors). Polymer Blends Handbook, 2<sup>nd</sup> edn. Amsterdam, Netherland: Elsevier; 2014.

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